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UTILIZATION OF SOYBEAN MEAL IN MOLDED PLASTICS

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More than 61 million pounds of phenolic resin was used in the manufacture of molding compounds during 1943 (11). Such molding compounds are usually produced by condensing phenol with formaldehyde to form a fusible resin and subsequently compounding the resin with an equal part of wood flour along with catalysts, lubricants, and coloring materials. With the return of competition to industry, manufacturers are turning to methods of reducing the cost of molding materials without lowering the quality of the finished product. The use of soybean meal offers one method of maintaining quality and reducing the cost since a substantial reduction in the amount of phenol required is achieved.

It has long been known that phenols and phenolic resins are compatible with soybean protein and soybean meal. Advantage has been taken of this fact to utilize the adhesive properties of soybean meal for supplementing those of phenolic resins in the phenolic resin-wood flour type of plastic (12). This development has enabled manufacturers to conserve the more expensive phenolic resin by replacing part of it with soybean meal.

The greatest problem involved in producing a plastic containing soybean meal is attainment of water resistance. Since soybean meal is highly water absorbent, it tends to impart this property to plastics when used as an ingredient. Treatment with formaldehyde improves the water resistance of soybean meal (3,4,6) but at the same time it decreases plastic-flow characteristics. Heat denaturation of the meal produces a material with increased water resistance and greater plasticity than formaldehyde-hardened meal when these materials are used with a phenolic resin (10).

Another problem is to avoid increase in curing time. Thermosetting materials are discharged from a hot die, while with thermoplastic materials the die must be cooled in order to set the plastic. Soybean protein is thermoplastic, provided a plasticizer is used (7). Phenolic resins in the early stage of condensation act as plasticizers for soybean meal (5,13). When the resin polymerizes to the insoluble, infusible state it no longer plasticizes the protein material and plastic flow stops. As a result the whole mixture sets up, giving a thermosetting plastic which may be removed from the hot die (9,10,14).

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Preparation of Meal

Oil-free soybean meal is not suitable for use in plastics without some modification. Soybean meal contains about 10 percent soluble sugars and also other soluble materials which decrease water resistance (8). Thus if the untreated meal is used, blistering is likely to result probably due to decomposition of sugars. Before use, untreated meal must be washed free of soluble materials. This washing must be carried out with water adjusted to the isoelectric point of the protein, pH 4.2 to 4.4, in order to prevent leaching out some of the protein. After washing out the soluble sugars the meal must be given a heat treatment to denature or insolubilize the protein. This denaturation is carried out in the laboratory by adjusting the moisture content of the meal to about 20 percent and heating under pressure at a temperature of 225° to 250° F. for 2 to 3 hours. If the pressure is released suddenly, most of the water escapes as vapor and the dry product obtained is suitable for use in plastics. Somewhat the same results may be obtained by drying the wet, leached meal at moderately high temperatures.

Either solvent extracted or screw-pressed meal is suitable for use in plastics. Screw-pressed meal ordinarily has been heated to the extent that it has been toasted, which tends to insolubilize the protein. On the other hand, the dark color of the meal limits its use to dark-colored plastics. Screw-pressed meal contains approximately 4 percent oil which acts as a lubricant, thus permitting a reduction in the amount of lubricant to be added to the molding material. Caution must be exercised when utilizing more than 10 percent of this type of meal because there is a tendency for the oil to exude if an excess is present.

When protein is extracted from soybean meal a residue is left that is free of water-soluble sugars but may contain from 35 to 50 percent protein (1,2). If this material is heat-denatured, it makes an excellent material for use in phenolic plastics.

Preparation of Molding Powder

Wet-mix Method.- The following formula is typical of methods used for preparing molding powders in the laboratory (10):

94 parts phenol (1 mole ratio)
56 parts leached soybean meal, heat-treated
5 parts hydrated lime
Mix well and allow phenol to soak into meal.
Add 122 parts 37-percent formaldehyde solution (1.5 moles).
Heat in closed, steam-jacketed mixer for 15 minutes with steam pressure of 20 pounds per square inch.
Heat 1 hour with jacket temperature of 190° to 210° F.
Add 112 parts wood flour,
1 part calcium stearate (may be reduced if screw-pressed meal is used),

1 part stearic acid,
11.66 parts hexamethylenetetramine (equivalent of 0.5 mole of formaldehyde).
Mix well and dry in air or vacuum at room temperature to a moisture content of less than 5 percent.
Work on hot calender rolls or in Banbury mixer for 1 to 3 minutes.
Grind to approximately 16 mesh to obtain molding powder.

The resin-forming reaction may be carried out in an autoclave or any steam-jacketed mixer which can be closed to prevent the escape of formaldehyde during the reaction. Drying may be accomplished by exhausting the air from the mixer or by spreading the material out for air drying.

The molding powder prepared by this method exhibited a plastic flow of from 0.70 to 1.40 inches, depending on the amount of rolling, when measured on the Rossi-Peakes flow tester at 700 p.s.i. and 150° C. (302° F.). The setting time determined by the flow tester under these conditions was approximately 90 seconds. The curing time, as determined by a cup molded at 300° F., was 2 minutes.

A number of modifications may be made in the formula given above in order to modify properties of the molding powder or of the finished plastic. For example, hydrated lime may be replaced by barium hydroxide, calcium oxide, barium oxide, or ammonia. Hexamethylenetetramine may be replaced by paraformaldehyde, and part of the phenol may be replaced by cresols. Part of the wood flour may be replaced by asbestos fiber in order to give a faster-curing molding powder or a finished plastic with increased heat resistance.

From the proportions of phenol and formaldehyde specified in the formula, approximately 112 parts of phenolic resin will be produced. Half as much soybean meal (56 parts) and 112 parts of wood flour are specified. Therefore, the molding powder will have a composition of approximately 40 percent phenolic resin, 20 percent soybean meal, and 40 percent wood flour. The properties of such a plastic compare favorably with those of a phenolic plastic containing 50 percent phenolic resin and 50 percent wood flour and offers a saving of 10 percent in resin content. The amount of soybean meal in the molding powder may be increased to 30 percent with proportionate decrease in phenolic resin. However, an increase in meal content gives a plastic of increased water absorption and lower flexural and impact strengths. The molding powder made with higher meal content usually requires longer curing time and more pressure for molding (10).

It should be noted that best results have been obtained by forming the resin in the presence of the soybean meal as described above. Success of this procedure may be accounted for by assuming that the protein reacts with the resin in some manner to form a perfectly homogeneous mass.

Dry-mix Method.- The conventional method for preparing phenolic-type molding powders involves making a fusible resin and grinding it with wood flour, catalysts, pigments, and lubricants in a ball mill. The powdered mixture is then compounded on hot calender rolls to obtain uniformity, and is again pulverized after cooling. The following formula is an example of this method in which 10 percent of treated soybean meal is used.

40	percent	two-stage phenolic resin
5	"	hexamethylenetetramine
40	"	wood flour
10	"	treated meal
2	"	hydrated lime
1.25	"	stearic acid
1.75	"	nigrosine dye
100 percent		

Ball mill 24 hours.

Roll for 3 minutes with cold roll at 120° F. and hot roll at 205° F.

This material gave a molding powder with a flow of 1.33 inches on the Rossi-Peakes flow tester at 500 p.s.i. and 150° C. The curing time was 90 seconds. These properties were comparable to those of a molding powder made with 50 percent resin and 45 percent wood flour, the remaining 5 percent being catalyst, lubricants, and dye as used in the above dry-mix formula (10).

Properties of the Plastic

A large number of molding powders have been made in the laboratory in which the resin, wood flour, and meal contents were varied. It was concluded that a leached, denatured soybean meal can be used to replace as much as 5 to 10 percent of the more expensive resin without altering appreciably the curing time and strength properties of the final plastic (10). Since the meal is only about 50 percent protein and the remaining 50 percent being inert, nonplastic material, 10 percent of meal must be used to replace 5 percent of resin and 5 percent of wood flour.

When soybean meal is used to replace wood flour, a strikingly large increase is noted in the plastic flow of the molding powder (10). In other words, a free-flowing molding powder may be produced by using 50 percent resin, 40 percent wood flour, and 10 percent treated meal or protein residue. Such free-flowing molding powders are usually made by using 60 percent resin and 40 percent wood flour.

With the introduction of electronic preheating equipment to the molding industry, molding powders or preforms are usually preheated before

molding. The effect of preheating phenolic molding material which has been modified with soybean meal is reported elsewhere (9,10). In general, the effect of preheating parallels that of straight wood flour-filled phenolics resulting in a corresponding reduction in the molding cycle.

The properties of the plastics produced from both the wet- and dry-mix formulas given above are as follows:

	Wet mix	Dry mix
Flexural strength, lbs./sq. in.	8,500 - 9,500	8,500 - 9,000
Impact strength, Izod, ft.-lbs./in. notch	0.35	0.32
Water absorption, 48 hrs., %	0.50	0.92
Specific gravity	1.39	1.37

Colored Plastics

Both phenolic resin and wood flour are difficult to dye, and colors are therefore usually obtained by using pigments. Soybean meal offers a protein base for dyeing. Tests under ultraviolet light show that phenolic plastics containing soybean meal are more stable to light than are those made without soybean meal when both kinds are colored with organic dyes. Color may be obtained as follows:

- Black - 2 percent nigrosine dye.
- Brown - 2 percent burnt umber and 1 percent brown dye.
- Red - 2 percent white clay and 2 percent Phenoform Red.
- Blue - 2 percent white clay and 1 percent Duratint Blue 1001.
- Green - 2 percent white clay and 2 percent green dye, Kohnstamm A6318.

Summary

It is possible to use 20 percent treated soybean meal with 40 percent phenol-formaldehyde resin and 40 percent wood flour without decreasing the quality of the plastic or adding undesirable properties to the molding powder, in comparison with a 50:50 mixture of resin and wood flour. Dyeing properties are definitely improved by the use of protein material from soybeans. Moreover, the use of the protein material makes it possible to decrease the phenolic resin content because of the increased flow obtained with the soybean protein thereby decreasing the cost of the finished product.

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